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essarily lead to a weakening of the N–N bond order. The N–N overlap population decreases from 1.19 in free N_2 (of identical internuclear separation) to 0.72 for the complexed N_2. Despite the rather important overlap population diminution, the N–N interaction is still strongly bonding. After interaction, the σ_{N-N}, π_{N-N}, and π^*_{N-N} orbitals are formally occupied while the σ^*_{N-N} orbital ($2a_u$) is vacant. Consequently, we conclude that there is an intracluster nitrogen–nitrogen bond in **1a** explaining the two electron deficiency.

When the N_2 ligand is replaced by acetylene (keeping the same bond distances) the HOMO–LUMO gap corresponding to the 64-electron count is somewhat reduced (0.98 eV), because of the weaker M–E antibonding character of the a_u MO, which becomes the LUMO in the acetylene case. Therefore, the existence of an hypercloso cluster of structure **1** having E = CR appears still possible, but such a cluster should be less stable than its N_2 homologue. Indeed, the presence of lone pairs on the E_2 ligand appears to be a stabilizing factor for such a molecule. Calculations in which the N–N and C–C separations vary from 1.15 to 1.50 Å lead to similar qualitative results.

It is generally admitted that dinitrogen, a better σ-donor than a π-donor, prefers to be coordinated in an end-on fashion rather than a side-on fashion. It is interesting to note that in **1a**, where N_2 is side-on complexed, *both* types of orbitals (σ lone pairs and π-bonding) are involved in the donation process to the metallic square.

Related and Known Structures

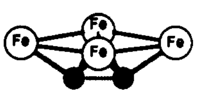
Intracluster main-group–main-group-bonding interactions have already been noticed in organometallic clusters. Five-vertex compounds $[W(CO)_5]_3(\mu_3\text{-}E_2)$ exhibit no metal–metal interactions but strong E–E bonding interactions. The E–E bond order is considered to be larger than 1.[4] A very short C–C contact of 1.275 Å is observed for the dicarbido unit complexed through a highly distorted metallic rectangle in the 70-electron compound $Ru_4(CO)_{12}(\mu\text{-}PPh_2)_2(\mu_4\text{-}C_2)$.[5]

Intracluster N-N bond observed in our hypothetical hypercloso complex **1a** is reminiscent of the situation encountered in the electron deficient $CpME_nMCp$ triple-decker complexes where a metal–metal bond is present through the inorganic E_n ring.[6] As in **1a**, electron deficiency in these hypercloso triple-decker species is attributed to the intracluster bond.

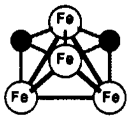
Note finally that with only one nitrogen atom, i.e., a *nido*-Fe_4N square pyramid, the situation is analogous to the one encountered for the Fe_4P_2 model **1b**. Rather large HOMO/LUMO gaps for the expected electron counts of seven and eight SEP's are computed (0.87 and 1.01 eV respectively).[1a,7]

Skeletal Isomers

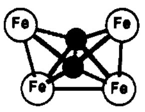
The PSEP theory[2] predicts alternative structures for 64-electron M_4E_2 clusters, based on the bicapped tetrahedron geometry, as shown in **2**. Our calculations indicate that, in fact, **2a** is unstable for any electron count.[8] A large HOMO/LUMO gap of 1.54 eV is calculated for **2b** with an electron count of 68, i.e. 4 electrons more than predicted by PSEP rules.[9] The **2c** model satisfies the PSEP rules since a HOMO/LUMO gap of 1.79 eV is observed with the favored 64-electron count. However, for this electron count, **2c**, which can be derived from **1a** by opening one metal–metal bond (a symmetry allowed process), is found unstable with respect to **1a**. Thus **1a** appears to be the only possible skeletal arrangement for a 64-electron six-vertex M_4N_2 organometallic cluster.



2a



2b



2c

Let us remark that cluster **1a** can be described from the condensation of a 40-electron M_2E_2 tetrahedron with a 24-electron M_2 organometallic fragment.[10] It is also structurally (and in some ways electronically) related to the 70-electron $[Co_4(CO)_{11}E_2]^{2-}$ (E = Bi, Sb) anions that adopt structure **2c**.[1c,11,12]

Finally, note that this type of hypothetical hypercloso cluster can be considered as an extention of the series of the compounds consisting of a μ_4-alkyne, -nitrile, or -azoalkane ligand coordinated to M_4 frameworks recently described and analyzed by Vahrenkamp et al.[13]

Computational Procedure

The calculations have been made within the extended Hückel formalism,[14] using the weighted H_{ij} formula.[15] The following bond distances (Å) have been used (see also text): Fe–C(O) = 1.85; C–O = 1.15; C–H = 1.09. The atomic parameters were taken from the literature.[1]

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(8) Such a E_2 coordination is observed in the 68-electron compound $Fe_2Ni_2(C_5H_5)_2(CO)_6(\mu_4\text{-}C_2Ph_2)$, whose metal atoms describe an almost flat distorted square: Sappa, E.; Manotti Lanfredi, A. M.; Predieri, G.; Tiripicchio, A.; Carty, A. J. *J. Organomet. Chem.* **1985**, *288*, 365.

(9) Though N and CH fragments are isolobal, their interaction with a tetrahedral $Fe_4(CO)_{12}$ unit leads to different MO diagrams. This difference is mainly due to their different electronegativity. Indeed, a HOMO/LUMO gap of 0.96 eV is computed for the expected electron count of 64 in $[Fe_4(CO)_{12}(\mu_3\text{-}CH)_2]^{2+}$ in agreement with the reported structure of $WOs_3(C_5H_5)(CO)_9(\mu_3\text{-}CTol)_2$: Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

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Hydride Locations and Bonding Studies in Some Silyl Polyhydride Rhenium Complexes

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Recently, Crabtree and his co-workers synthesized and characterized several rhenium polyhydride complexes.[1,2] Although the positions of the heavy atoms in these rhenium complexes were determined by X-ray crystallography, the positions of the H atoms are unknown. Crabtree and his co-workers based suggested structure for these complexes on NMR spectroscopy. For example, a pentagonal-bipyramidal structure was proposed for the 7-coordinate complex $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si, Sn), where the two H atoms are located in the equatorial plane. For $ReH_6(SiR_3)(PPh_3)_2$, a classical 9-coordinate tricapped trigonal-prismatic structure was proposed with the two PPh_3 ligands and the silyl group occupying the three equatorial sites, i.e. the

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capping sites. Accurate locations of H atoms can be obtained experimentally through neutron diffraction technique, but one needs larger well-formed crystals and long collection times. Alternatively, as we have shown, quantum mechanical calculations can be used to locate hydride positions in metal complexes.[3]

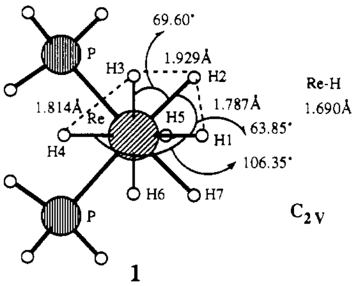
In this paper, ab initio molecular orbital calculations with analytical gradients were employed to locate the positions of the H atoms in these two rhenium hydride complexes and to discuss the detailed electronic interactions between rhenium and ligands and possible Si···H interactions. Our approach is to use the X-ray structures to fix the positions of all the heavy atoms and to use energy gradient optimization techniques to find the positions of H atoms. All aryl and alkyl groups were replaced by H atoms. These substituting H atoms were also fixed by using standard bond lengths and bond angles.[4]

Theoretical Details

All geometries were optimized at the restricted Hartree–Fock level. Ab initio effective core potentials were employed in all calculations. The core electrons of Re were fitted to an effective core potential (ECP1), while valence electrons were described with a double-ζ basis (3s3p3d/2s2p2d).[5] The core of Re is the [Xe] configuration. For ligand atoms, the effective core potentials and basis sets of Stevens, Basch, and Krauss were used.[6] The basis set for H consisted of a three-Gaussian contraction from which the most diffuse component was split off to form a double-ζ basis.[7] All calculations were performed with the GAMESS package.[8] The valence electron density and its Laplacian were plotted with the use of the program MOPLOT.[9] All GAMESS calculations were made at the Cornell National Supercomputer Facility on an IBM 3090-600VF computer and at the Supercomputer Center of Texas A&M University on a Cray Y-MP2/116 computer.

Results and Discussions

$ReH_7(dppe)_2$. To examine the accuracy of the ab initio method in these calculations, we optimized the 9-coordinate rhenium hydride $ReH_7(PH_3)_2$, fixing the $Re(PH_3)_2$ unit in accordance with the X-ray structure, restricting the symmetry to C_{2v} and keeping all Re–H bond lengths equal. The detailed structural parameters from this optimization are shown in **1**. We compared this optimized structure with a real rhenium hydride complex ReH_7(ddpe)[10] [dppe = 1,2-bis(diphenylphosphino)ethane] determined structurally by neutron diffraction. The structure of ReH_7(dppe) (see also **1**) was described either as a distorted tricapped trigonal prism with the phosphorus atoms occupying two eclipsed position and H1, H4, and H5 occupying the three capping positions or as a monocapped square antiprism with H1 capping the H2H3H6H7 square plane. The Re–H bond lengths range from 1.66 to 1.69 Å, and there are no intramolecular H···H separations less than 1.77 Å. In the model complex, the optimized Re–H bond length is 1.69 Å and the closest H···H separation is 1.79 Å. This result gives us confidence that we can use the same MO method to predict the unknown hydride complexes.



1

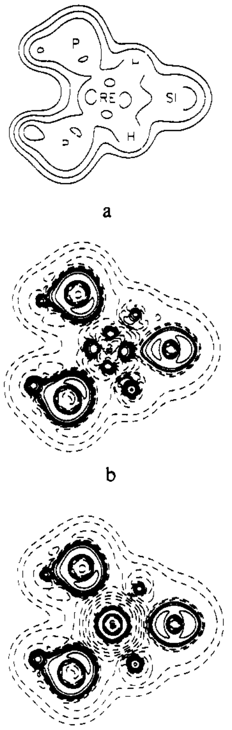
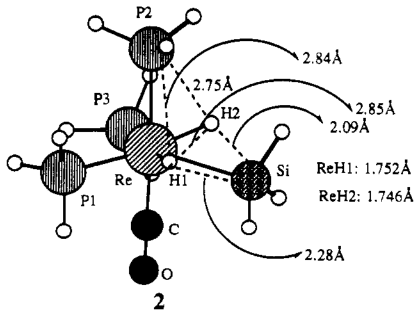


Figure 1. Plots of ρ(ECP1) (a), $-\nabla^2\rho$(ECP1) (b), and $-\nabla^2\rho$(ECP2) (c) on the approximate equatorial plane (described in the text) of the model complex $ReH_2(SiH_3)CO(PH_3)_2$ (see **2**).

$ReH_2(SiPh_3)(CO)(PMe_2Ph)_3$. The X-ray crystal structure of $ReH_2(SiPh_3)(CO)(PMe_2Ph)_3$ indicated that the ReP_3CSi core is a distorted trigonal bipyramid if the two hydrides are ignored.[1] The PReP angle in the equatorial plane is about 104°, which is far less than 120° for an ideal trigonal bipyramid and far larger than 72° for an ideal pentagonal bipyramid. Therefore, no simple ideal coordinate polyhedron summarizes the observed bond angles. The optimized model complex $ReH_2(SiH_3)(CO)(PH_3)_3$, shown in **2**, indicates that it can be described either as a distorted pentagonal-bipyramidal structure or as a distorted bicapped (capping the two PSiP faces) trigonal-bipyramidal structure (the detailed structure will be described below).



2

To examine the detailed H···Si and Re–Si interactions, we plot the total valence electron density ρ and its Laplacian, $-\nabla^2\rho$,[11,12] on an approximate equatorial plane of the distorted pentagonal bipyramid where the two hydrides are above the plane (0.26 and

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[9] Interactive MOPLOT: a package for the interactive display and analysis of molecular wavefunctions incorporating the programs MOPLOT (D. L. Lichtenburger), PLOTDEN (R. F. W. Bader, D. J. Kenworthy, P. M. Beddal, G. R. Runtz, and S. G. Anderson), SCHUSS (R. F. W. Bader, G. R. Runtz, S. G. Anderson, and F. W. Biegler-Koening), and EXTREM (R. F. W. Bader and F. W. Biegler-Koenig), P. Sherwood and P. J. MacDougall, 1989.

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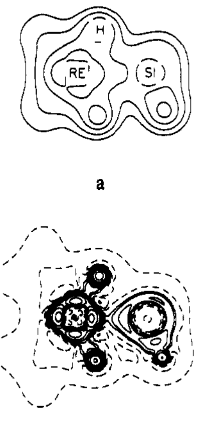
0.35 Å), the two phosphines are below the plane (0.15 and 0.27 Å), the Re atom is exactly on the plane, and the Si atom is below the plane (0.52 Å). The plots of ρ and its Laplacian, $-\nabla^2\rho$, on this plane are shown in Figure 1a,b. In the contour displays of the Laplacian of the electron density, solid lines denote $-\nabla^2\rho > 0$, where the electron charge is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, where the electron charge is locally depleted. It can be seen from Figure 1b that the two phosphines and the two hydrides are bonded to the Re through the depletions around the central atom, as is usual for dative bonds. On the other hand, two concentrations (one on silicon, the other on rhenium) appear between Re and Si atoms, as is usual for covalent bonds. Interestingly, the two hydrides are opposite minima in the valence-shell charge concentration of the silicon atom. Apparently, these minima exert weak attractions toward hydrides.

Geometrically, we found long Re–H bonds (compared to 1.69 Å in **1**) and short Si···H (2.1–2.3 Å) distances. This result also suggests that there are weak interactions between Si and H atoms since the Si···H distances are much shorter than the sum of the van der Waals radii of silicon and hydrogen (3.3 Å) but not as short as that (1.802 Å) in the Mn(μ_2-H)Si unit of the (η^5-$CH_3C_5H_4$)$(CO)_2$(H)MnSiF$(C_6H_5)_2$ complex.[13] The positions of the two hydrides are clearly shifted toward the Si atom. For example, in the optimized structure **2**, H1-Re-Si and H2-Re-Si angles are 63.17 and 56.72°, respectively, while H1–Re–P1 and H2–Re–P3 angles are 72.10 and 69.30°. We also optimized the model complex $ReH_2(SiH_3)CO(PH_3)_3$ by fixing the Si, the Re, and the two phosphines (P1 and P3; see **2**) on the equatorial plane with a mirror plane passing through the P2–Re–CO–Si atoms and angle of 100° for P1–Re–P3. The result gives a Re–H bond distance of 1.739 Å and a P2–Re–H bond angle of 84.16°. Again H atoms are closer to Si atom than P1 (and P3). The dihedral angle between the P2–Re–H and P2–Re–Si planes is 58.79° while the one between the P2–Re–H and P2–Re–P1 planes is 66.21°.

Using this idealized geometry but rotating the SiH_3 group by 180° about the Re–Si axis, we optimized the model complex again. The result gives a Re–H bond distance of 1.733 Å and a P2–Re–H bond angle of 88.58°. The dihedral angle between the P2–Re–H and P2–Re–Si planes is 59.53°, which is smaller than the one between the P2–Re–H and P2–Re–P1 planes (65.47°). This structure is energetically higher than the previous one by 2.3 kcal/mol. The hydrides are again close to the silicon atom and are located almost in the equatorial plane in the latter structure. Thus, the orientation of the three aryl groups of $SiPh_3$ in the complex plays a significant role on the positions of the two hydrides, but the Si···H interactions exist for all of these distortions.

All these observations lead us to suggest that the Si···H interactions are significant and are related to the large P–Re–P angle, 104° rather than 72°. These interactions also prevent the ReP_3CSi core from undergoing Berry pseudorotation as pointed out by Crabtree and co-workers.[1] Capping the two hydrides on the two PSiC faces[1] is unfavorable from the result of our optimized structure. The two hydrides lying above the equatorial plane (see **2**) allow a maximum interaction between Si and H atoms because of the orientation of the three aryl groups of $SiPh_3$ in the $ReH_2(SiPh_3)(CO)(PMe_2Ph)_3$ complex.

We also examined the effect of 5s and 5p electrons of Re atom on our analyses of the electron density above through an ab initio molecular orbital calculation on the optimized structure **2** using another effective core potential (ECP2) where the 5s and 5p electrons are taken as valence electrons.[14] The plot of $-\nabla^2\rho$ on the approximate equatorial plane of the distorted pentagonal bipyramid described above is shown in Figure 1c. The nonspherical charge distribution (four maxima and four minima) in the central metal atom (see Figure 1c) results apparently from the addition of the spherical $5s^2$ and $5p^6$ electron density and the very nonspherical 5d valence electron density. The locations of the four maxima in the charge concentration of the central atom (see Figure 1c) are qualitatively equivalent to those observed in Figure 1b. The concentrations in the ligand atoms are essentially the same as those in Figure 1b.

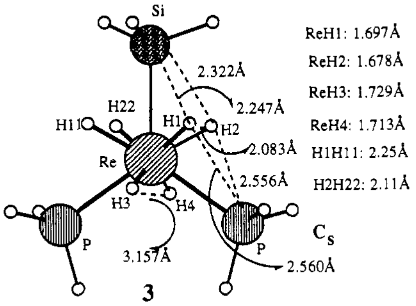


a

b

Figure 2. Plots of ρ(ECP1) (a) and $-\nabla^2\rho$(ECP1) (b) on the ReSiH1 plane of the model complex $ReH_6(SiH_3)(PH_3)_2$ (see **3**).

$ReH_6(SiR_3)(PPh_3)_2$. The spectroscopic and X-ray diffraction studies suggest that $ReH_6(SiR_3)(PPh_3)_2$ has a classical 9-coordinate tricapped trigonal-prismatic structure with the SiR_3 and the two PPh_3 ligands occupying the equatorial sites. The optimized model complex is shown in **3**. We found that there are four hydrides surrounding the Si atom with distances in the range 2.2–2.3 Å. The H···P (ca. 2.56 Å) distances are longer than the H···Si distances. These four hydrides are magnetically distinct from the other two. This explains the experimental observation of a 2:4 ratio of the two hydride resonances in the ^1H NMR spectrum. The optimized structure also confirms the proposed geometry of Crabtree and his co-workers.[2] The plots of total valence electron density and its Laplacian in ReSiH1 plane (H22 is almost in the same plane) are shown in Figure 2a,b. From Figure 2, we can see that the Re–Si bond is also covalent as in the $ReH_2SiR_3(CO)(PPh_3)_3$ complex. Moreover, Re–H bonds have more covalent bond characteristics than those in the $ReH_2SiR_3(CO)(PPh_3)_3$ complex. This result can be easily understood by comparing the number of hydrides in these two rhenium complexes. The fewer number of hydrides a metal complex has, the easier the metal donates its electrons to them. Weak Si···H interaction can be also deduced from the shape of the electron concentration on the Si atom (see Figure 2b). The hydrides are opposite minima [(3, +1) critical points in the $-\nabla^2\rho$ plot] in the valence-shell charge concentration of the silicon atom.



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Summary. In summary, the available geometry optimization technqiues within standard ab initio molecular orbital programs allow us to easily locate the position of H atoms in these hydride complexes. The analyses of total valence electron density show that these two silyl polyhydride rhenium complexes have significant covalent character in the Re–Si bond and weak Si···H interactions. Unlike the other ligand atoms, the silicon is less electronegative, and therefore the silyl radical group (SiR_3) easily donates its bonding electron to the metal–silicon bonding region, forming a significantly covalent bond. As a result of transfering its electron to the central metal atom, silicon has the additional weak bonding ability to attract the hydrides.

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Dinuclear Pt(II), Pd(II), Ni(II), and Cu(II) Complexes of 3,5-Pyrazoledicarboxylic Acid

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and Melanie M. Gumz[‡]

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There is much current interest in dinuclear metal complexes from the standpoint of catalysis,[1] biological mimicry,[2] multielectron-transfer reactions,[3] and metal–metal interactions.[4] Among ligands capable of forming dinuclear complexes, there has been a very strong interest in pyrazoles.[5–10] This heterocycle has been extensively employed in pyrazolylborates,[11] to stabilize a variety of organometallic and coordination compounds. In much of the recent work, interest has focused on the ability of the pyrazole ring to hold two metals ions in close proximity and on controlling the properties of the metal ion by the substitution at the 3- and 5-positions.

We have become particularly interested in the 3,5-dicarboxypyrazoles, which are easily synthesized.[12] These planar, heteroaromatic dicarboxylates have a number of attractive features. They are sterically compact, allow metal–metal interactions through π orbitals, and can carry substantial negative charge. In view of these features they have been investigated surprisingly little although there have been significant studies on *pyrazine*-dicarboxylates, which have yielded a number of interesting compounds.[13] In the five-membered diaza ring system we have shown that the imidazoledicarboxylates can form trianionic planar chelates with two metal ions under appropriate conditions.[14] However, the pyrazoledicarboxylates hold the metal ions even closer. Here we report synthetic and structural results on complexes of 3,5-pyazoledicarboxylic acid (H_3Dcp) as a dinucleating, trianionic ligand.

Complexes of this ligand, with metals that can sustain square-planar coordination, can result in planar dinuclear anions. Not only can such ions potentially stack and undergo partial oxidation but they can be precipitated with cations that are themselves capable of forming anisotropic conductors or that are magnetically active. The resulting products should resemble the better known mononuclear systems, which lead to one-dimensional metals in the case of oxalates and cyanides[15] and magnetic chains in the case of copper complexes.[16] The feature of planar metal–metal interaction in addition to the stacking interaction may lead to interesting modifications of physical properties.[17]

Experimental Section

$(NBu_4)_2[Pt_2(Dcp)_2]$ was prepared by dissolving 3,5-dicarboxypyrazole monohydrate (Fluka) (160 mg, 0.92 mmol) in 20 mL of hot water. The solution was mixed with 0.46 mmol of H_2PtCl_4 in 10 mL of water. Addition of 1.78 mL of NBu_4OH (40% in water) (2.76 mmol) produces a mixture of white and red precipitates. Addition of 10 mL of acetonitrile dissolves the red precipitate, presumably $(NBu_4)_2PtCl_4$. Reduction of solvent volume by half followed by cooling leads to precipitation of a white solid. Recrystallization from acetonitrile–water yields 120 mg (45%) of analytically pure product. IR (KBr pellet): $\nu(COO)_{as}$ 1647 cm^{-1}. Anal. Calcd for $C_{42}N_6H_{74}O_8Pt_2$: C, 42.71; H, 6.31; N, 7.11. Found: C, 42.96; H, 6.23; N, 7.31.

Table I. Summary of Crystal Data for Complexes $(NBu_4)_2[M_2(Dcp)2]$ (M = Pd, Cu)

	$(NBu_4)_2[Pd_2(Dcp)_2]$	$(NBu_4)_2[Cu_2(Dcp)_2]$
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.290 (3)	10.899 (4)
b, Å	11.893 (4)	12.286 (5)
c, Å	10.775 (3)	9.899 (3)
α, deg	107.95 (3)	109.51 (3)
β, deg	100.05 (3)	101.88 (3)
γ, deg	113.26 (2)	102.69 (3)
V	1187.7 (7)	1161.3 (8)
Z	1	1
cryst dimens, mm	0.36 × 0.31 × 0.17	0.31 × 0.18 × 0.42
calcd density, g cm^{-3}	1.40	1.31
abs coeff, cm^{-1}	15.15	9.42
formula	$C_{42}H_{74}N_6O_8Pd_2$	$C_{42}H_{74}N_6O_8Cu_2$
fw	1003.9	918.2
radiation, Å	0.71069	0.71069
no. of unique rfls	4202	3066
no. of obs rfls ($F_o^2 \geq 3\sigma(F_o^2)$)	3583	2374
R	0.048	0.043
R_w	0.048	0.044

$(NBu_4)_2[Pd_2(Dcp)_2]$. A 100-mg sample of $PdCl_2$ (0.56 mmol) and 1.47 mg of 3,5-dicarboxypyrazole monohydrate (0.84 mmol) were stirred in 20 mL of hot water. When all the solids had dissolved, 1.27 mL (1.95 mmol) of NBu_4OH (40% in water) was added, producing a yellow precipitate. Recrystallization from acetonitrile–water yields shiny yellow

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